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NON-EQUILIBRIUM PROCESSES IN INTERSTELLAR MOLECULES

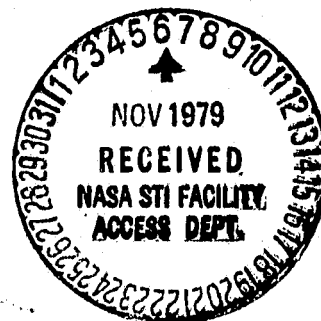
(NASA-TM-75685) NON-EQUILIBRIUM PROCESSES
IN INTERSTELLAR MOLECULES (National
Aeronautics and Space Administration) 27 p
HC A03/MF A01 CSCL 09B

N80-10981

Unclas
G3/90 45875

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Translation of "Neravnovesniye Protesessy v
Mezhzvezdnykh Molekulakh", Academy of Sciences
USSR, Institute of Space Research, Moscow, Report
Pr-462, 1979, pp. 1-30.



NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D. C. 20546
October, 1979

As is well known, thermodynamic equilibrium is an asymptotic concept that is unattainable in a strict sense. In sufficiently dense astrophysical objects (in stars, for example), local thermodynamic equilibrium (L.T.E.) is probably achieved to a first approximation. For this, at each point of space the translational velocities of the particles are described by a Maxwell distribution, the populations of discrete energy levels by a Boltzmann distribution, and the ionization and dissociation by a Saha distribution, all with a single value T of the temperature, but the temperature changes from point to point and, furthermore, the radiation field can differ from the equilibrium value by any amount. The indicated equilibrium distributions can be established only for the condition that a detailed balance of all the quantum transitions occurs. The translational motion of the particles, which is "made Maxwellian" most easily, performs the "leading part" in the establishment of LTE, since the velocities of the chaotic motions of the particles are usually determined by their mutual elastic collisions and not by other processes. Under such conditions for thermalization (that is, for bringing the gas into a state that is characteristic for LTE) of the other degrees of freedom of the gas, it is sufficient that these degrees of freedom be controlled by the collisions, that is, that the transitions between the corresponding energy levels occur significantly more frequently as the result of collisions than from other causes. /4

The concentrations of particles in the interstellar gas clouds are insufficient for collisional thermalization of the majority of the energy levels of the molecules. Only the lowest levels, between which radiative transitions occur more rarely than collisional transitions even at the comparatively low densities, turn out to be the best cases of thermalization. If some part of the levels is thermalized, then one calls such a state "partial LTE".

*Numbers in margin indicate foreign pagination.

In some cases transitions that are induced by the equilibrium 2.7 degree radiation of the universe (the primeval fireball background) can become the dominant processes in the replenishment and emptying of certain levels. The populations of such levels are also thermalized; they are described by the Boltzmann equation with a temperature $T=2.7$ K.

Another situation, where the probabilities of transitions under the action of collisions and of the radiation field are comparable, is attained considerably more frequently in the interstellar clouds. Then the "competition" of the collisional and radiative processes can lead to any distribution of the populations, since collisional and radiative transitions are subject to different selection rules. Just such extremely non-equilibrium situations will be the subject of discussion in this article.

Let us introduce some concepts which are useful for the analysis of non-equilibrium processes in interstellar molecules.

It is convenient to characterize the ratio of the populations of two arbitrary levels 1 and 2 (for definiteness let us assume that Level 2 is the upper one) by means of the excitation temperature,

$$T_{\text{ex}} = \frac{E_2 - E_1}{k \ln \frac{n_2}{n_1}} \quad (1)$$

where n_1 and n_2 are the populations of the levels (the number of molecules in a given level per cm^3 divided by the statistical weight of the level), ΔE is the energy difference between the levels, and k is the Boltzmann constant. /5

In the general case the molecules are located in the environment of a Maxwellian gas with a kinetic temperature T_K and in a radiation field with a temperature T_r . We shall call the ratio of the populations of the two levels non-equilibrium if $T_{\text{ex}} \neq T_K$. If there are a total of two levels in the system ($m=2$), then T_{ex} always lies between T_K and T_r :

$$T_{\text{ex}} \in [T_K, T_r] \quad (2)$$

One can be convinced of the correctness of this almost obvious statement after solving a system of steady-state equations for the two levels. And if $m > 2$, that is, exchange by the populations of these two levels (we shall call them "signal" levels) with other levels is possible, then a violation of Condition (2) is possible in principle. Here one of the following situations is realized:

- 1/ $0 < T_{0x} < T_K, T_T$;
- 2/ $0 < T_{0x} < T_{0x}^{(1)} < T_{0x}^{(2)} < T_T$;
- 3/ $T_{0x} < 0$.

The transition from Level 1 to Level 2 is called "anomalously cooled" in Case 1 and "anomalously heated" in Case 2. In these two cases the excitation temperature goes out beyond the limits of the interval bounded by the temperatures of the two "thermostats" with which the molecules interact, remaining, however, positive. But, as is evident from Equation (1), the excitation temperature can also be negative (Case 3) if $n_2 > n_1$. (Of course, this does not contradict any physical principles; of course, T_{ex} is not a physical temperature, but is just a convenient parameter to describe the distribution of the molecules over the energy levels). Case 3 is called the "population inversion" or the "inversion of the transition from Level 1 to Level 2". As Equation (1) shows upon the onset of the inversion, T_{ex} changes with an abrupt jump from $+\infty$ to $-\infty$ and, for a further increase of the relative population of the upper level, it increases monotonically, approaching zero from the direction of negative values. /6

The specific processes which lead to a non-equilibrium distribution of the populations of the levels are called "pumping processes". Case 3 is of special interest, since a population inversion is a necessary and sufficient condition for the appearance of maser amplification of the emission for a given transition.

The interstellar medium is a unique "laboratory" in which one can find regions with the most diverse relations of the probabilities

for collisional and radiative transitions. Therefore, both cases of thermalization of the molecular transitions by collisions (or by the 2.7-degree background) and also all three cases of the non-equilibrium relation of the populations are observed here.

It is relevant here to turn our attention to the failure of the terms "anti-inversion" and "anti-maser effect" with which one often characterizes Case 1. Actually a break in the continuous change of T_{ex} occurs upon the inversion of the populations; here a qualitatively new effect, the maser amplification of the emission, appears abruptly. For the anomalous cooling of the transition (Case 1'), there is nothing similar; here there are no singular points in the change of T_{ex} . Therefore, Case 2 (of the anomalous heating transition) is an analogy to Case 1, but Case 3 is not.

Each of the two opposite cases, thermalization and non-equilibrium state, is of interest from the point of view of possibly extracting astrophysical information from the observations. But the second case is considerably more sensitive to model selection than 17 is the first. If one is certain that a given transition is thermalized, then the excitation temperature of the transition derived from the observations (for an optically thick cloud, the temperature simply equals the brightness temperature at the center of the line) directly determines the kinetic temperature of the gas (or the temperature of the equilibrium background radiation). Furthermore, in the case of collisional thermalization, one can immediately estimate a lower limit for the gas concentration from the condition that the populations of the levels are controlled by collisions and not by radiative transitions.

If a strongly non-equilibrium nature is indicated for the population distribution, then a detailed analysis of the possible pumping mechanism is necessary. In this case the physical conditions in the cloud are determined indirectly by the selection of that pumping model which describes the observed properties of the lines in the best manner. But the strongly non-equilibrium cases are of interest

from another point of view, too; they demonstrate the vast diversity of the specific physical situations in the interstellar clouds, which lead to the attainment of powerful heat engines on a "cosmic" scale.

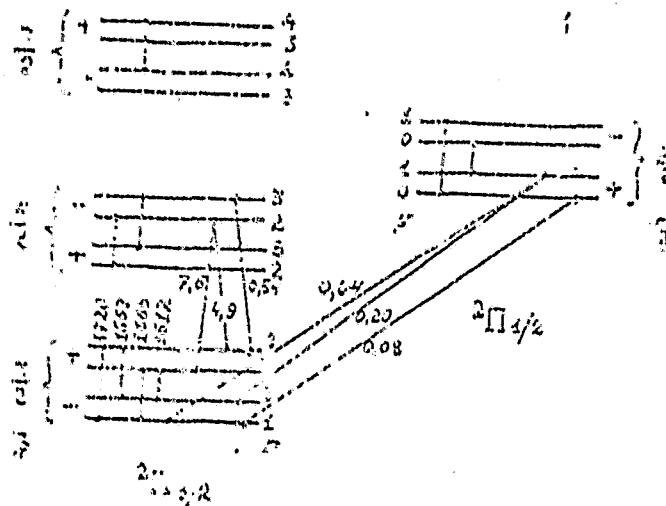
The main observational manifestations of the extremely non-equilibrium processes proceeding in interstellar and circumstellar clouds are briefly examined in the following chapter, and in Chapter III are the elements of the theory for these processes. One can find more detailed information in the symposium [1], in the author's survey [2] and in the monograph [3].

CHAPTER II. The Observations

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The fact that, in the rarefied interstellar clouds, the populations of the discrete energy levels are, as a rule, non-equilibrium, has been well-known for a long time. Furthermore, starting from the general properties of the interstellar medium, some researchers predicted the possibility of such radical effects as population inversion and maser amplification several years before the discovery of cosmic masers (see, for example, [4], page 494). And, nevertheless, when the molecular cosmic masers were actually discovered, the scales of the directed energy transformation processes occurring in them surpassed all expectations.

The first maser sources for OH molecules were discovered in 1965 (see [5]). Now the number of known sources exceeds 150. Radio lines which arise in transitions between the sublevels of several low rotational levels in the ground electronic and vibrational state are observed in emission.



sity of the emission and k is the Boltzmann constant. The brightness temperature of thermal emission cannot be greater than the kinetic temperature. In the case of just the OH emission lines, the brightness temperatures reach $\sim 10^{13}^\circ\text{K}$, whereas the kinetic temperatures of the emitting gas, judging from the observed line widths are $T_K \lesssim 100^\circ\text{K}$. This already indicates that the radio transitions of OH are overheated to a very strong degree by some pumping mechanism, that is, the emission is not thermal. But will one possibly succeed in explaining such a high emission intensity without resorting to the hypothesis of maser amplification, that is, by remaining in the region of positive excitation temperatures? /10

Two circumstances do not allow one to do this. First, are the observed small dimensions of the OH sources: the condensations which emit separate Doppler details in the spectrum have diameters from $\sim 10^{14}$ to 10^{15} cm, and the distances between them are $\sim 10^{16}$ cm. This indicates that the size L of the emitting condensation along the line of sight cannot be $> 10^{16}$ cm in order of magnitude. Second, the allowable concentration of any particles in the region of emission is limited by the observed line widths: for concentrations $n \gtrsim 10^{13} \text{ cm}^{-3}$, collisional broadening becomes larger than the observed widths. Even more rigid limitations on the total concentration of particles ($n \lesssim 10^9$ to 10^{10} cm^{-3}) result from an analysis of the possible pumping mechanisms (Chapter III).

With allowance for these two facts, we attempt to explain the observed brightness temperatures without going out beyond the limits of positive excitation temperatures. After solving the usual equation of transfer for a one-dimensional medium and going over from intensity to brightness temperature, we shall find that, at outflow from the medium, the brightness temperature in the center of the line is

$$T_B = T_{0K} (1 - e^{-\tau}), \quad (4)$$

where τ is the optical thickness of the medium at the central frequency of the line:

$$\tau = \alpha L = \frac{\lambda^2 A_{12} n_2 \Delta E_{12}}{8\pi h \nu \Delta \nu} L, \quad (5)$$

α is the absorption coefficient, A_{12} is the Einstein coefficient /11 for the probability of a spontaneous transition, and $\Delta \nu$ is the line width. We neglected the background radiation, since its brightness temperature is insignificant in comparison with the brightness temperature of the OH lines. Further, since T_{ex} is very great then, as is evident from Equation (5), τ must be small. It is easy to be convinced that $\tau \ll 1$ for any reasonable values of the quantities which enter into Equation (5). This is an effect of "clearing" of the medium that is connected with an increase of the role of induced emission at large values of T_{ex} . For $\tau \ll 1$, Equation (4) gives $T_B \approx T_{\text{ex}} \cdot \tau$ or, taking Equation (5) into account,

$$T_B \approx \frac{\lambda^2 A_{12} \Delta E_{12}}{8\pi h \nu \Delta \nu} n_2 L. \quad (6)$$

Thus, at very large T_{ex} values, the brightness temperature ceases to depend on T_{ex} . This one again is a result of "clearing" of the medium. Actually, we shall obtain exactly the same expression for T_B as Equation (6) after simply summing in the necessary manner all the events of the molecules' spontaneous emission (with allowance for the fact that for $kT_{\text{ex}} \gg \Delta E_{12}$ the populations n_1 and n_2 are practically equal). Substituting into Equation (6) values of the parameters that are typical for OH sources ($\lambda \sim 18$ cm, $A_{12} \sim 10^{-11}$ sec $^{-1}$, $\Delta E = 1.1 \cdot 10^{-17}$ erg, $\Delta \nu \sim 10^3$ Hz, $T_B \sim 10^{13}$ K), we shall find $n_1 L \sim 10^{27}$ cm $^{-2}$ and, allowing for the fact that $L < 10^{16}$ cm, we shall obtain $n_1 > 10^{11}$ cm $^{-3}$. Since only a part of the OH molecules are found in Levels 1 and 2, the total concentration of these molecules must be still higher. As far as the concentration of hydrogen atoms (or molecules) is concerned, for a normal cosmic abundance of oxygen $[O]/[H] \sim 7 \cdot 10^{-4}$, it will then be at least three orders of magnitude higher than the concentration of OH molecules, that is, for certain, it will exceed the maximum allowable value of $n \sim 10^{13}$ cm $^{-3}$.

Thus, it is impossible to explain the observed intensities of the OH lines by only the spontaneous emission of the molecules; the conclusion that the emission in these lines undergoes significant amplification inside the source appears to be inescapable. /12

It is necessary for amplification that the absorption coefficient become negative which, as is evident from Equation (5), can be achieved only with a negative value for T_{ex} (that is, by a population inversion), since all the other quantities which determine α are significantly positive.

Although the very authors of the discovery of the OH emission sources, astounded by the sharply non-equilibrium ratio of the intensities of the superfine radio line components, decided that a part of the lines is not emitted by OH but by some other material (the famous "Mysterium"; see [5]), many researchers very quickly and obviously independently of each other suggested the concept of maser amplification in a medium with an inverted population of the levels to explain the features of the OH lines which were observed. Not only the enormous intensities of the OH emission but also other unusual properties of this emission, in particular, the high degree of polarization and its marked unsteadiness find a natural explanation in the framework of this concept. In some cases the emission is 100% circularly polarized. As far as variability is concerned, the line intensities, the line profiles and the parameters of polarization are subject to it. The characteristic times of variability are months or weeks.

Emission with similar properties at a frequency of 22.2 GHz, which corresponds to a single radio transition of the H_2O molecule (the $6_{16} - 5_{23}$ rotational transition), was discovered in 1968 in the direction of many OH sources (see [6]).

A diagram of the rotational energy levels of H_2O is shown in Figure 2. H_2O sources are characterized by still smaller dimensions (some condensations have an observed diameter of $\sim 10^{13}$ cm), /13

by higher brightness temperatures (up to 10^{15} K), by more pronounced unsteadiness, but by a smaller degree of polarization and, moreover, only linear polarization is observed.

The brightest of the OH and H₂O sources are closely associated with well-known astrophysical objects; with strong ionized hydrogen regions, with high luminosity cool stars that have strong excesses of infrared radiation (the infrared stars), and also with infrared sources which do not show up in the optical range. The OH and H₂O sources that are observed in the direction of HII regions gravitate towards the densest and most compact condensations of ionized hydrogen which, from all signs, are young HII regions which did not succeed in expanding and are surrounded by recently born hot stars.

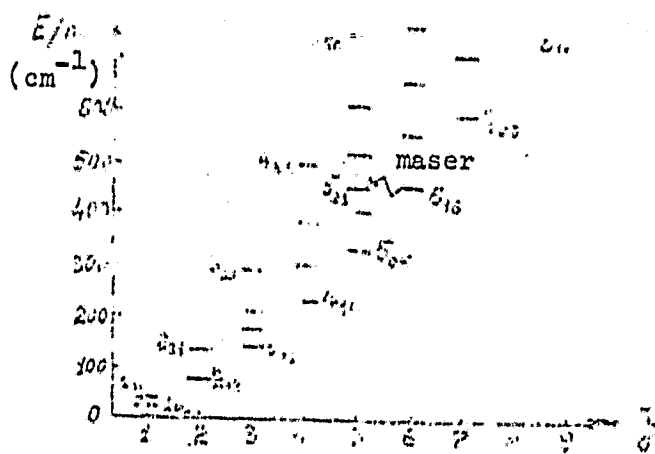


Figure 2

The spectrum of a maser source that is associated with a HII (ionized hydrogen) region at first glance appears to be a chaotic superposition of narrow lines (their equivalent Doppler width is ~ 1 km/sec) that are scattered over tens and sometimes over hundreds of km/sec in radial velocity. Radio interferometric observations with very long baselines have allowed one to determine that, to each narrow detail in the spectrum there corresponds a separate bright condensation on the sky with a diameter from

10^{13} to 10^{15} cm. The condensations are grouped into nests with typical dimensions of $\sim 10^{16}$ cm which are scattered on a general area with a diameter of $\sim 10^{17}$ cm. The intensity changes of the spectral components are sometimes correlated in broad intervals of the spectrum. On the other hand, intensity variations in opposite phases were noticed for details that are very close in radial velocity.

If one assumes that each maser condensation associated with an HII region radiates isotropically, then the radiation power of the H_2O condensations turns out to be within the limits from 10^{30} to 10^{33} ergs/sec, and the radiation power of the condensations of OH is from 10^{27} to 10^{29} ergs/sec. One must emphasize that the assumption of isotropic radiation for individual condensations does not affect the estimate of the total power for the source: after assuming that each condensation radiates anisotropically into a solid angle of Ω steradians, we must suppose that the observed condensations (whose radiation beams are randomly oriented in the direction of the Earth) amount to a $\Omega/4\pi$ part of the total number of condensations, so that the total radiation power has the same equal effect as for the assumption of isotropy for the individual radiators. The indicated luminosities of the maser sources are comparable with the luminosities of dwarf stars, but it is necessary to allow for the fact that maser sources emit all their power in a narrow spectral line. The number of resonance radio photons emitted by the source appears to be enormous: from $\sim 10^{45}$ to $\sim 10^{49}$ photons/sec.

The spectra of sources that are associated with infrared stars have a more regular structure. These sources emit most strongly in the 1612 MHz line of OH (the $J = 1 \rightarrow J = 2$ transition in the state $2_{\pi 3/2}$, $F = 3/2$). Two groups of Doppler details that are separated by an interval of 10 to 50 km/sec are observed in the 1612 MHz line. The emission in the other OH lines and in the H_2O line is usually situated within the interval. The interferometric observations showed that the maser condensations which correspond to individual

spectral details are included in an extensive region with a typical diameter of $\sim 10^{16}$ cm which evidently appears to be a flattened gas and dust envelope around the infrared star.

The majority of infrared stars belong to the class of long-period variables. It has been noticed that the OH and H₂O maser emission, as a rule, changes its intensity in phase with the changes of the infrared flux from the star. However, individual cases of anticorrelation of the fluxes of the maser and infrared radiation are observed (see [7]).

The luminosities of the maser sources associated with the infrared stars are, on the average, less than those for sources associated with HII regions and usually do not exceed $\sim 10^{45}$ photons/sec both in the OH line and in the H₂O line.

Compact sources of silicon monoxide (SiO) maser emission were discovered very recently (see [8]). These sources are unique in the sense that they emit from excited vibrational molecular states. Rotational transitions were observed both in the first and second excited vibrational states, whose excitation energies are, in temperature units, $\sim 1800^\circ\text{K}$ and $\sim 3500^\circ\text{K}$. The SiO sources are very closely associated with the H₂O sources; particularly, a very close coincidence of their radial velocities is observed. Observations of emission from excited vibrational states indicate general excitation of the molecules in the SiO and H₂O sources. All transitions that /16 have been observed in excited vibrational SiO states reveal signs of maser amplification.

The OH, H₂O, and SiO maser sources are a special group of molecular sources. All of them are no doubt closely related with individual stars or protostars. They have compactness of the radiating condensations and a high power of the pumping mechanisms, which act in a small volume.

Signs of maser amplification or of strong overheating of the radio transitions are observed in the emission of a number of other

molecules (CH_3OH , CH , HC_5N), but, by all probability, these are sources of an entirely different type; they are considerably more extensive, they are not so clearly associated with starlike objects, and they have significantly less pumping power.

The "anti-inversion" phenomenon (we shall use this term which we have grown accustomed to for the sake of brevity, remembering, however, what was said in connection with this in a previous discourse) is observed only in extensive interstellar clouds. Absorption in the radio line of the formaldehyde (H_2CO) molecule at a wavelength of $\lambda 6.2$ cm was discovered in 1969 in many directions in the galaxy (see [9]). This line, being formed for transitions between the 1_{11} and 1_{10} rotational levels (see Figure 3) is almost always observed in absorption, even in those cases where, in the direction of the absorption, even in those cases where, in the direction of the absorbing cloud, there is no known radio source whatsoever with a continuous spectrum which could serve as a "hot" background. In such a situation, only the universal cosmic background (the primeval fireball radiation), whose brightness temperature amounts to a total of only 2.7°K , can be absorbed. Since the H_2CO molecules absorb this radiation, the excitation temperature of the 1_{11} - 1_{10} transition must be lower than 2.7°K .

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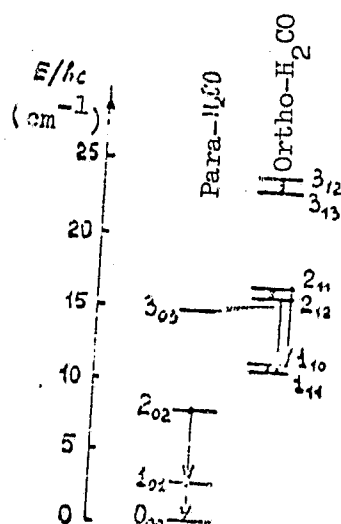


Figure 3

But the kinetic temperature in the interstellar clouds is, for certain, higher than 3°K (this has been determined from observations of the radio lines of other molecules); consequently, the indicated transition of formaldehyde is "anti-inverted". The phenomenon of "anti-inversion" is also observed in OH radio transitions in extended, dense interstellar clouds and in the atmospheres of comets.

CHAPTER III. The Theory

1. The Thermodynamics of Cosmic Masers and "anti-masers"

In the operation process of a cosmic maser or "anti-maser", cyclical energy transformations occur; therefore, one can consider a maser or an "anti-maser" as some heat engine. A thermodynamic analysis allows one to develop in a clear form the general laws governing the operation of a cosmic heat engine and to formulate some general requirements for any pumping model.

As was already said, anomalous cooling, anomalous heating, or the inversion of some transition 1-2 are possible only in the presence of an exchange by the populations with "external" layers. Here the sequence of the elementary processes which provide for non- equilibrium populations can be fairly complex, but the directed transfer of populations between the signal levels is always the final result. The fundamental diagrams for the operation of the cosmic heat engines are depicted in Figure 4. Here the set of levels that are external in relation to the signal transition 1-2 and situated either higher than (the left-hand diagrams) or lower than (the right-hand diagrams) the signal transition has been conditionally denoted by the number 3. Transitions which do not occur in reality are shown by thin arrows, and they only show the direction of the resulting transfer of the populations. The diagram once more convinces one of the fact that, in each pumping diagram, the presence of both a source and of a discharge of energy is required. /19

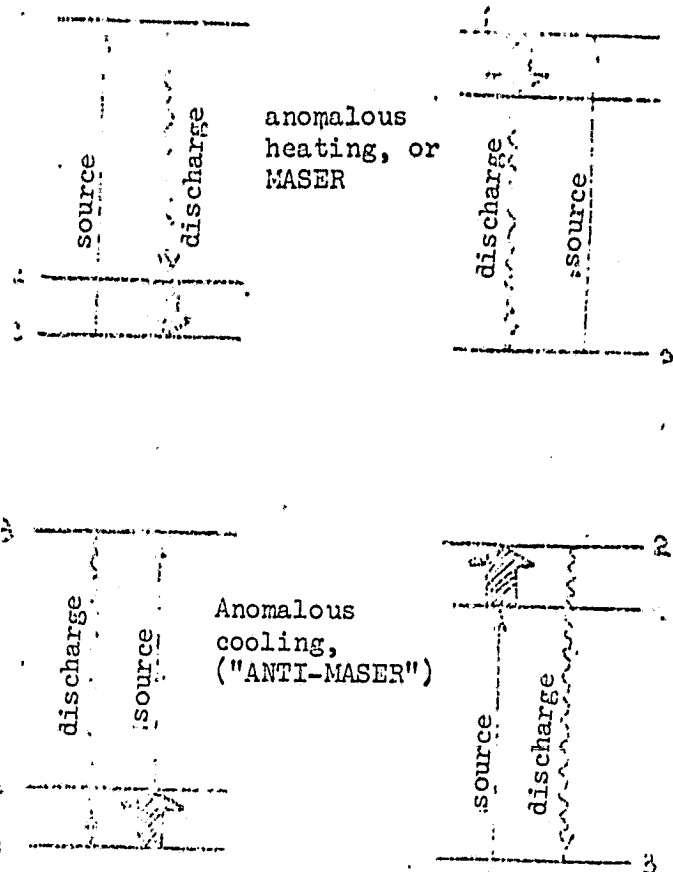


Figure 4. Diagrams for the operation of cosmic heat engines.

1,2 are the signal layers; 3 is a "generalized" external layer.

As for every heat engine, the source must be hotter than the discharge. If the source and discharge are not in equilibrium, then their temperatures are understood to be a parameter which characterizes the energy density near those energies which correspond to the quantum transitions of the "working" molecules. As usual, the higher the temperature of the sources T_s and the lower the temperature of the discharge T_d , the higher is the efficiency of the process:

$$\text{eff.} \leq 1 - (T_d/T_s). \quad (7)$$

Furthermore, the quantum nature of the cycle for a cosmic heat engine allows one to formulate some additional requirements of a

general nature which the pumping mechanism must satisfy. For example, if a radiation field is the energy discharge, then, as is evident from Figure 4, each maser photon emitted by the medium (or each photon of cold radiation absorbed in the medium in the case of "anti-inversion" requires the "annihilation") (the exit from the medium or a true absorption within the medium) of at least one discharge photon. Similar conditioned firm up the requirements presented for each model of pumping.

2. The models of pumping for cosmic masers and "anti-masers". /20

The mechanisms of pumping are usually classified according to the source of energy. In this sense there are three types of pumping that are conceivable for molecules:

- 1) Radiative,
- 2) Collisional, and
- 3) Chemical.

The primary excitation of the molecules is accomplished by emission for radiative pumping, as the result of inelastic collisions for collisional pumping, and as the result of chemical reactions for chemical pumping. One usually calls pumping "chemical" if the non-equilibrium nature of the populations appears as a result of a chemical reaction although, strictly speaking, in the case of endothermic reactions, the source of the excitation energy for the molecules is not chemical energy but the energy of the collision which led to the reaction. One can also say the same thing about photochemical reactions; one often calls the mechanisms of pumping based on them "chemical", although, in the strict sense, according to the source of energy, they are radiative.

In the majority of the models of pumping that have been suggested, the non-equilibrium populations of the signal levels arise as a result of the cascade transitions of molecules from levels that are situated higher up, where the molecules end up as a result of the primary excitation by the source of pumping. During cascade

transitions photons are emitted which provide for the discharge of energy. For all such pumping mechanisms, there exists a limitation on the total density of particles; this results from the requirement that the collisions do not hinder the cascade transitions of a molecule. If n is the total concentration of the exciting particles, v is the velocity of their motion with respect to the working molecules, and $\sigma(v)$ is the cross-section of an intramolecular transition under the effect of a collision, then $n \overline{v\sigma}$ is the probability coefficient for a collisional transition (sec^{-1}) and the indicated requirements are written as: /21

$$n \overline{v\sigma} < A_c \quad (8)$$

or

$$n < A_c / \overline{v\sigma}, \quad (9)$$

where A_c is a typical value for the probability coefficient of one element of a cascade transition, and a line over the terms indicates averaging with respect to velocities.

For example, the cascade transitions over the rotational levels that are often invoked in pumping models are characterized by a spontaneous decay probability $A_c \sim 0.1$ to 1 sec^{-1} ; for collisions with neutral atoms and molecules at temperature $T_K \sim 10^2$ to 10^3 K $\overline{v\sigma} \sim \overline{v} \times \sigma \sim 10^{-10} \text{ cm}^3/\text{sec}$, and for collisions with electrons $\overline{v\sigma} \sim 10^{-7} \text{ cm}^3/\text{sec}$. In this case, we find from Equation (9) that the concentration of neutral particles in the region of pumping cannot exceed $\sim 10^9$ to 10^{10} cm^{-3} , and the concentration of electrons cannot be greater than $\sim 10^6$ to 10^7 cm^{-3} .

It is evident from the diagrams depicted in Figure 4 that all the radiative mechanisms of pumping must satisfy the requirement: for each "maser" photon, there is a minimum of one pumping photon. This requirement often turns out to be an insurmountable difficulty for radiative models that are satisfactory in other respects.

In its turn, each collisional mechanism must satisfy the con-

dition: for each "maser" photon, there is a minimum of one collisional excitation, that is,

$$n_m \geq \frac{N_s}{V} \quad (10)$$

where N_s is the total number of "maser" photons emitted for the sources in a unit of time n_m is the concentration of working molecules, and V is the volume of the source. Condition (10) determines the lower limit of the product of the concentration of exciting particles and of working molecules: /22

$$n_m n \geq \frac{N_s}{V} \quad (11)$$

Thus, the collision mechanism, as a rule, turns out to be efficient only in a fairly narrow interval of concentrations that is determined by the set of Conditions (9) and (11).

In light of what was said above about the important role of energy discharge, it appears to be expedient to classify pumping mechanisms not only according to the type of source, but more fully, according to the combination of the source and discharge. One can then divide the pumping mechanisms that have been suggested up until now into the following groups: collisional-radiative, radiative-radiative, and radiative-collisional.

Let us examine several specific examples.

The mechanism suggested by the author in [10] and independently by R. Hills (see [1], pp 64-66) serves as an example of the collisional-radiative mechanism of pumping for H_2O maser sources. This is its essence. For concentrations of hydrogen atoms (molecules) which do not exceed $\sim 10^9 \text{ cm}^{-3}$, the H_2O molecules which collide with them go over into excited rotational states that are situated higher than the working levels 5_{23} and 6_{16} , but they return back not as a result of collisions, but mainly by means of spontaneous cascade transitions along the ladder of rotational levels. The basic cause of the inversion which occurs here for the $6_{16}-5_{23}$ transition

is different in those positions which the 6_{16} and 5_{23} levels occupy in the groups of levels with their own values of the rotational quantum number J , that is, in the groups $J=6$ and $J=5$ respectively. Specifically, the 6_{16} level is lower in its J -group /23 whereas the 5_{23} level occupies the middle position in its J -group. The selection rules permit only one "strong" spontaneous transition from any level lower in its J -group: to the next lower level of the neighboring J -group. Thanks to this property, molecules must be accumulated in the lower levels if, during collisions, they are excited into fairly high levels and are deactivated by means of cascade transitions. Actually, if a molecule fell into any one of the lower levels at some stage of the cascade transition, then, from then on, it will be lowered only along the lower levels, that is, it is seemingly "captured" by the set of these levels. In other words, there exists a directed transfer of the populations into the set of the lower levels from the set of the remaining levels, thanks to which the populations of the lower levels turn out, on an average, to be higher than the populations of the levels adjacent to them. In particular, the population of the 6_{16} level can exceed the population of the 5_{23} level, that is, a transition that is necessary for us will turn out to be inverted. This pumping mechanism was investigated in detail in [11] and [12]. Collisions do not absolutely have to be the primary source of excitation of the molecules. It can, for example, be the chemical reaction $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H} + 0.69 \text{ eV}$, which leads to the formation of rotationally excited H_2O molecules.

In order to provide the observed brightness temperatures for a H_2O maser emission, the number of inverted molecules in the line of sight in a column of unit cross-section (a quantity which one can call the "projected density") must be no less than 10^{16} cm^{-2} (see [2]). The projected density of the molecules for each rotational level in the vicinity of the signal levels will be of the very same order of magnitude: $n_2 \sim 10^{16} \text{ cm}^{-2}$. Since the effective cross-section for H_2O molecules for the absorption of rotational /24 photons $k_2 \sim 10^{-14} \text{ cm}^2$, the maser condensations must be optically thick in the rotational lines ($\tau_2 = n_2 L k_2 \gg 1$). Multiple scattering

of the rotational photons hinders their outflow from the medium. Goldreich and Kwan [13] concluded on this basis that collisional pumping of H_2O does not have an effective energy discharge and cannot operate in the most powerful sources. One may not regard this conclusion as final. First, for an elongated geometry of the maser condensations, a fairly effective outflow of the photons is possible in directions with low optical thickness. Second, if the dust in the region of pumping is colder than the gas (which is very probable), then it turns out to be an effective absorber of infrared photons and, in principle, cannot only provide for the necessary energy discharge, but can also shift the balance of the quantum transitions in the molecules in the direction of increasing the inversion for the $6_{16}-5_{23}$ transition (see [14] and [15]). True, if the emission of the powerful maser condensations is isotropic, then relative concentrations of dust that are two to three orders of magnitude greater than in ordinary interstellar clouds are required. (There is an error in the example shown in [14]: one must increase the relative concentration of dust particles to $\sim 10^{-10}$. This error led the author to a false conclusion about the incorrectness of the expression for the rate of annihilation of photons on dust that has been suggested in [13].

As an example of the radiative-radiative mechanism, let us examine the mechanism of infrared pumping for OH sources that has been suggested by I. S. Shklovskiy [16] and studied in more detail by M. Litvak [17]. The resonance emission in the rotational or vibrational-rotational OH lines from an external source is the source of the primary excitation for the molecules here. However, the immediate cause of the appearance of inversion for some transitions or other between the sublevels of the $^2\pi_{3/2}, \gamma = 3/2$ ground state are the multiple scattering features of photons in the rotational lines which connect this state with the two nearest rotational states $^2\pi_{3/2}, \gamma = 5/2$ and $^2\pi_{1/2}, \gamma = 1/2$. Each pair of sublevels with the given parity (+, -) of the ground state is connected by three permitted transitions with a pair of sublevels of an excited state with the opposite polarity.. This is shown in

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Figure 1 for the lower components of the Λ -doublets of the ground state and of the $^2\pi_{1/2}$, $\tilde{\gamma} = 1/2$ state and for the upper components of the Λ -doublets of the ground state and of the $^2\pi_{3/2}$, $\tilde{\gamma} = 5/2$ state. Pumping is accomplished thanks to "coupled" lines which have a common upper level. Because of a difference in the line strengths the photons in the "coupled" lines are scattered differently in a cloud: in individual parts of a cloud a relative accumulation of photons in the strong line occurs and in other parts the opposite occurs. The absorption of "excess" photons with subsequent re-emission of "deficient" photons leads to an effective transfer of populations between the superfine sublevels of the ground state.

The nature of the population transfer depends significantly on whether or not the superfine line components overlap, that is, on the ratio of the line widths to the value of the superfine splitting of the levels. If the lines do not overlap, the transfer of the populations is identical for the upper and lower pairs of a Λ -doublet, since the strengths of the lines connecting these pairs with the sublevels of the excited states are identical. As a result an overpopulation of either the upper or lower superfine sublevel occurs that is identical for both components of the Λ -doublet. It is easy to consider that pumping here operates only in relation to the satellite lines: either the 1612 MHz transition turns out to be "overheated" and the 1720 MHz transition is "supercooled", or vice versa, but the principal lines remain unaffected.

If such a partial overlap of the superfine line components occurs, then pumping effects are also possible for the principal lines. The values of the superfine splitting differ fairly strongly for different components of the Λ -doublets, and, therefore, the degree of overlap of lines can be greatly different for transitions from the sublevels of the upper and lower components of the Λ -doublet. In this case the transfer of populations between the superfine sublevels can have an entirely different nature for the upper and lower components of the Λ -doublet.

Such a situation, for example, is possible where, for the upper component, the lower sublevel will turn out to be overpopulated, and for the lower component, the upper sublevel is overpopulated. Then the principal line at 1665 MHz will be amplified.

The radiation field in definite components of the rotational lines is the energy discharge for such infrared pumping. The question about the adequacy of the discharge in this mechanism of pumping has not yet been investigated. It is possible that definite difficulties will arise here. In this case the discharge is significantly local: crudely speaking, it occurs for those superfine components of a transition whose radiation field in this source region turned out to be "colder" than the radiation field of the other components because of the effects of multiple scattering that have been described above. The typical dimensions of a region in which the discharge favors inversion of a given transition in any case must be less than the typical distances between individual emitting condensations with different radial velocities: $R < 10^{15}$ cm. The total number of photons in the discharge line leaving /27 the region of pumping cannot be greater than the number which a region of great optical thickness with the same dimensions emits:

$$L_c < \frac{16\pi^2 \nu^3 (\Delta\nu/\nu) R^2}{c^2} \left(1 - e^{-h\nu/kT_{ex}} \right), \quad (12)$$

where T_{ex} is the temperature of the emission in the discharge line and $\Delta\nu/\nu = \Delta v/c$ is the relative Doppler width of the line. The excitation temperature of the OH rotational transitions probably does not exceed the kinetic temperature which, judging from the widths of the OH maser lines (with allowance for possible narrowing because of exponential amplification; see [2]), must not be greater than 500°K. Substituting such a value of T_{ex} and the corresponding value $\Delta\nu/\nu \approx 2 \cdot 10^{-6}$ into Equation (12), we shall obtain $L_c < 3 \cdot 10^{43}$ photons/sec. At the same time, the maser luminosity of the individual condensations in the most powerful OH sources exceeds this value by at least several times (assuming isotropic emission;

see [1] through [3]). Anisotropy of the radiation (an elongated geometry for the condensations, for which the maser emission flows out from the "ends" and the discharge photons flow out in lateral directions) can save the situation. Unlike collisional-radiative pumping that has been described above, in this case invoking cold dust as a discharge appears to be unpromising, since dust will absorb both the discharge photons and also the source photons to approximately the same degree, which will simply lead to a decrease of the pumping power.

Let us just consider the example of the radiative-collisional mechanism of pumping for H_2O sources suggested by Goldreich and Kwan [13]. The mechanism operates if the dust in the region of pumping is hotter than the gas, which can, for example, occur periodically in the vicinity of a cool variable star whose radiation rapidly heats the dust particles but not the gas. The infrared emission of the heated dust, which induces transitions of the molecules from the ground state into excited vibrational states, serves as the source of pumping and collisions of the excited molecules with particles of the cold gas, which lead to radiationless reverse transitions into the ground vibrational state, are the discharge. The authors did not investigate the total balance of transitions in the H_2O molecules which interact with the infrared radiation; they only showed that the infrared emission of the dust drains off molecules from the 5_{23} level more frequently than from the 6_{16} level. If one assumes that collisional deactivation from an excited vibrational state refills these levels at approximately the same rate, then the entire cycle must lead to an inversion of the $6_{16}-5_{23}$ transition. This scheme is satisfactory from a thermodynamics point of view; there is both an energy source and discharge. But the point is that, in reality, the process described will not control the populations of the signal levels; during the interaction of the H_2O molecules with the quasi-equilibrium infrared emission, an effective exchange by the populations of each rotational level with a large number of other levels is unavoidable, and not an exchange with some one level; therefore, the cycle described "drowns" /28

among a great many others. Furthermore, calculations show that the total balance of transitions in the H_2O molecules which interact with the quasi-equilibrium infrared emission has just cooling of the $6_{16}-5_{23}$ transition as its result and not heating of it (see [11] and [18]).

In the mechanism of Goldreich and Kwan, as also in all other models of pumping that have been suggested until now, it is /29 required that the total concentration of particles not exceed $\sim 10^9 \text{ cm}^{-3}$ (in this case this is connected not with the suppression of cascade fluorescence, but with the unacceptably rapid equalization of the dust and gas temperatures for $n > 10^9 \text{ cm}^{-3}$). However, if one eliminates the unlikely assumptions of strong anisotropy for the sources and of their physical dimensions being much larger than the observed interferometric dimensions, then one succeeds in reconciling the enormous emission intensities of the most powerful sources with the indicated upper limit for the density only at the price of the assumption that the working molecules themselves make up a significant fraction of all the particles in the zone of amplification (see [19]). Although one may not consider this assumption as absolutely unrealistic, of course it appears to be fairly artificial. It is more likely that the H_2O and OH molecules are only a small admixture to the H_2 molecules and are markedly less in concentration than such stable molecules as, for example, CO . But then, to provide the necessary numbers of working molecules, one must assume that the total concentration of particles in the zone of amplification is significantly greater than 10^9 cm^{-3} and most likely is no less than 10^{11} to 10^{12} cm^{-3} . At present the author is investigating the possibility of cosmic maser pumping at such high densities.

As a rule, the correct investigation of the pumping mechanism is a laborious process (especially if one must allow for multiple scattering of the photons). In this case, however, "the game is worth the risk", because a more profound understanding is "being gained" of the very distinctive physical processes which go on in cosmic heat engines.

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